Transition Metal-Ethylene Complexes as High-Capacity Hydrogen Storage Media

E. Durgun,[1, 2] S. Ciraci,[1, 2, *] W. Zhou,[3, 4] and T. Yildirim[3, 4]

[1]*Department of Physics, Bilkent University, Ankara 06800, Turkey*
[2]*UNAM - National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey*
[3]*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg MD 20899*
[4]*Department of Materials Science and Engineering, Univ. of Pennsylvania, Philadelphia, PA 19104*
(Dated: February 6, 2008)

From first-principles calculations, we predict that a single ethylene molecule can form a stable complex with two transition metals (TM) such as Ti. The resulting TM-ethylene complex then absorbs up to ten hydrogen molecules, reaching to gravimetric storage capacity of $\sim$14 wt%. Dimerization, polymerizations and incorporation of the TM-ethylene complexes in nanoporous carbon materials have been also discussed. Our results are quite remarkable and open a new approach to high-capacity hydrogen storage materials discovery.

PACS numbers: 73.63.Nm, 72.25.-b, 75.75.+a

Hydrogen is considered as one of the best alternative and renewable fuels[1, 2] due its abundance, easy synthesis, and non-polluting nature when used in fuel cells. However, the main concern is the safe storage and efficient transport of this highly flammable gas[3].

The main obstacles in hydrogen storage are slow kinetics, poor reversibility and high dehydrogenation temperatures for the chemical hydrides[4]; and very low desorption temperatures/energies for the physisorption materials (metal-organic frameworks (MOF)[5], carbide-derived carbons (CDC)[6], etc). Recently, a novel concept to overcome these obstacles have been suggested[7, 8, 9, 10, 11, 12, 13, 14]. It was predicted that a single Ti-atom affixed to carbon nanostructures, like C_{60} or nanotubes, strongly adsorbs up to four hydrogen molecules[7, 8, 10]. The interaction between hydrogen molecules and transition metals is very unique, lying between chemi and physisorption, with a binding energy of 0.4 eV compatible with room temperature desorption/absorption. The origin of this unusual "molecular chemisorption" is explained by well-known Dewar coordination and Kubas interaction[15]. The transition metals (TM) are chemically bonded onto different molecules/nanostructures through hybridization of lowest-unoccupied molecular orbital (LUMO) of nanostructure with TM d-orbitals (i.e. Dewar coordination). The resulting complex then binds multiple molecular hydrogens through hybridization between $H_2-\sigma^*$ antibonding and TM d-orbitals (i.e. Kubas interactions).

Synthesizing the predicted structures of Ti decorated nanotubes/C_{60} were proven to be very difficult due to lack of bulk quantities of small-diameter nanotubes and strong C_{60}-C_{60} interactions in the solid phase. Moreover, Ti atoms uniformly coating the SWNT/C_{60} surface may be subject to clustering after several charging-discharging process[16].

In search for a more efficient and feasible high capacity hydrogen storage medium, we found that the C=C double bond of an ethylene molecule C_2H_4, mim-
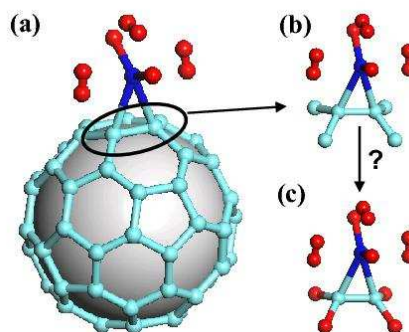

FIG. 1: (color online) (a) One of the most stable structure of Ti-C_{60} complex where Ti atom (blue) is bonded to a double bond with four hydrogen molecules attached (red). (b) The local structure of the Ti-C_{60}-double bond. (c) Replacing the end carbon atoms shown in (b) by H results in an ethylene molecule. This suggests that we may simple use ethylene molecule to hold Ti atoms, which then binds multiple hydrogen molecules.

ics double bonds of C_{60} that strongly binds TM-atom (see Fig. 1) and therefore it is expected to support TM atoms strongly to provide a basis for high-capacity hydrogen storage via the Dewar-Kubas mechanism discussed above.

In this letter, we explored this idea and indeed found that a single ethylene molecule can hold not only one but two Ti atoms, i.e. $C_2H_4Ti_2$, which then reversibly binds up to ten H_2 molecules yielding an unexpectedly high storage capacity of $\sim$ 14 wt %. These results suggest that ethylene, a well-known inexpensive molecule, can be an important basis in developing frameworks for efficient and safe hydrogen storage media.

Our results are obtained from first-principles plane wave calculations within density functional theory using Vanderbilt-type ultra-soft pseudopotentials with Perdew-Zunger exchange correlation[17]. Single molecules have
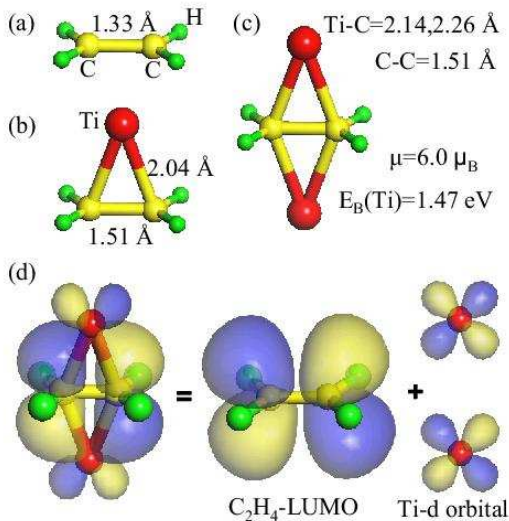
FIG. 2: (Color online) Optimized structure of an ethylene molecule C_2H_4 (a), C_2H_4Ti (b), and $C_2H_4Ti_2$ (c). The panel (d) shows that Ti-C_2H_4 bonding orbital results from the hybridization of the LUMO of the C_2H_4 and the Ti-d orbital, in accord with Dewar coordination.

been treated in a supercell of $15 \times 15 \times 15$ Å with Γ k-point and a cutoff energy of 408 eV. The structures are optimized until the maximum force allowed on each atom is less than 0.01 eV/Å for both spin-paired and spin-relaxed cases.

We first studied the bonding of a single Ti atom to an ethylene molecule to form C_2H_4Ti (see Fig. 2(b)). We found no energy barrier for this reaction. The binding energy is calculated by subtracting the equilibrium total energy E_T of C_2H_4Ti molecule from the sum of the total energies of free ethylene molecule and of Ti atom; $E_B(Ti)=E_T(C_2H_4)+E_T(Ti)-E_T(C_2H_4Ti)$. The Ti atom forms a symmetric bridge bond with the C=C bond of ethylene with $E_B = 1.45$ eV. Interestingly, it is also possible to attach a second Ti atom to the C_2H_4Ti to form $C_2H_4Ti_2$ (see Fig. 2(c)) without any potential barrier and about the same binding energy as the first Ti atom. In the optimized structure (Fig. 2(c)), each Ti atom is closer to one of the carbon atoms, leading to two different Ti-C bonds. Fig. 2(d) shows that the bonding orbital for the Ti-atoms and C_2H_4 results from the hybridization of the LUMO orbital of the ethylene molecule and the Ti-d orbitals, in accord with Dewar coordination[15]. The spin-polarized calculation gives 1.53 eV lower energy than non-spin-polarized one, suggesting magnetic ground state for $C_2H_4Ti_2$ with moment $\mu = 6\mu_B$ per molecule.

The stability of the $C_2H_4Ti_2$ complex were further tested by normal mode analysis. We found no soft (i.e negative) mode. There are three main Ti-modes. In two of these modes, Ti atoms vibrate parallel and perpendicular to the C=C bond and have the energies of 176 cm^{-1} and 123 cm^{-1}, respectively. In the third Ti-mode

Ti atoms vibrate perpendicular to the C_2H_4 plane with energy of 367 cm^{-1}. These three modes are unique for the $C_2H_4Ti_2$ complex and therefore should be present in any Raman/IR spectra of a successfully synthesized material.

We next studied the H_2 storage capacity of Ti-ethylene complex, by calculating the interaction between $C_2H_4Ti_2$ and different number of H_2 molecules and configurations. The first H_2 molecule is absorbed dissociatively to form $C_2H_4(TiH_2)_2$ as shown in Fig. 3(a) with a binding energy of 1.18 eV/H_2. The additional hydrogen molecules do not dissociate and molecularly absorbed around the Ti-atom. Two of these configurations are shown in Fig. 3(b) and (c). In $C_2H_4(TiH_2-2H_2)_2$ configuration, two H_2 are molecularly bonded from left and right side of the TiH$_2$ group with a binding energy of 0.38 eV/H_2 and significantly elongated H-H bond length of 0.81 Å. It is also energetically favorable to add a third H_2 molecule from the top of the TiH$_2$ group, with a binding energy of 0.4 eV and bond length of 0.82 Å. The resulting structure, $C_2H_4(TiH_2-3H_2)_2$, is shown in Fig. 3(c). We note that these binding energies have the right order of magnitude for room temperature storage. Since the hydrogens are absorbed molecularly, we also expect fast absorption/desorption kinetics.

Finally, we also observed many other local stable configurations where all of the hydrogen molecules are bonded molecularly. One of such configuration, denoted as $C_2H_4(Ti-5H_2)_2$, is shown in Fig. 3(d). Here the H_2 molecules stay intact and benefit equally from bonding with the Ti atom. The total ten hydrogen molecules absorbed by a single Ti-ethylene complex, $C_2H_4(Ti-5H_2)_2$, corresponds to a ~ 14 wt % gravimetric density, which is more than twice of the criterion set for efficient hydrogen storage. By removing the top H_2 molecule, we find that $C_2H_4(Ti-4H_2)_2$ configuration is also a local minimum and have a slightly (0.08 eV/H_2) higher energy than the $C_2H_4(TiH_2-3 H_2)_2$ configuration shown in Fig. 3(c). Our MD simulations indicate that the system oscillates between these two configurations. This is consistent with the observation that in Kubas compounds[15], the dihydrogen (i.e 2H) and molecular (i.e H_2) bonding are usually found to be in resonance[15].

The top hydrogen molecule in $C_2H_4(Ti-5H_2)_2$, has the weakest bonding in the system with $E_B=0.29$ eV while the side H_2 molecules have the strongest bonding with $E_B=0.49$ eV/H_2 and significantly elongated H-H bond distance of 0.85 Å. This suggests the presence of two different H_2-$C_2H_4Ti_2$ bonding orbitals as shown in Fig 3(e) and (f). The first one is the hybridization between the top-H_2 σ^*-antibonding and the Ti-d orbital. The second one is the simultaneous hybridization of the side H_2 σ^*-antibonding orbitals with the Ti-d orbital. Since the bonding orbitals are mainly between metal $d-$ and hydrogen σ^*-antibonding orbitals, the mechanism of this interesting interaction can be explained by the Kubas
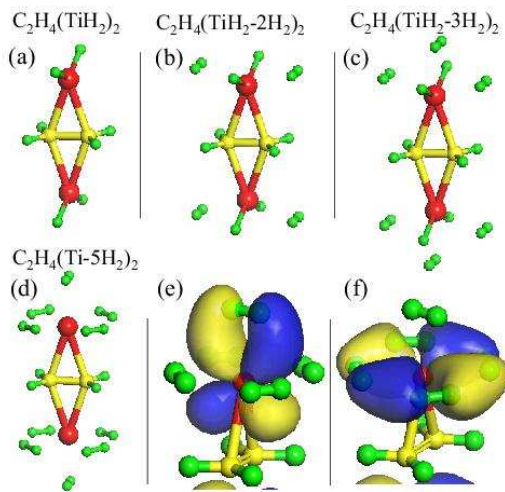
FIG. 3: (Color online) Atomic configurations of an ethylene molecule functionalized by two Ti atoms, holding (a) two H_2 molecules which are dissociated, (b) six H_2 molecules, and (c) eight H_2 molecules. Panel (d) shows a configuration where ten H_2 are bonded all molecularly. The spin-polarized calculations gave lower energies (in eV) by 1.5, 0.37,0.16, and 0.06 for configurations shown in (a)-(d), respectively, suggesting magnetic ground state for all cases with moment of $\mu \approx 2\mu_B$. The panel (e) and (f) shows the bonding orbital for the top (e) and side hydrogen molecules, respectively. Note that the hydrogen σ^*-antibonding orbitals are hybridized with Ti-d-orbitals, suggesting Kubas interaction for the H_2-Ti bonding.

interaction[15].

We also calculated the normal modes of C_2H_4(Ti-$5H_2$)$_2$ and did not find any soft modes, indicating that the system indeed corresponds to a local minimum. Among many vibrational modes, we note that the H_2 stretching mode is around 2700-3000 cm^{-1} for side H_2 and around 3300 cm^{-1} for top H_2 molecules, significantly lower than the 4400 cm^{-1} for free H_2 molecule. Such a shift in the mode frequency would be the key feature that can be probed by Raman/IR measurement to confirm a successful synthesis of the structures predicted here.

Finally, the stability of C_2H_4(Ti-$5H_2$)$_2$ structure has been further studied by carrying out *ab-initio* molecular dynamic calculations performed at 300 K and 800 K. While all ten H_2 molecules have remained bound to C_2H_4Ti$_2$ molecule at 300 K, they start to desorb above 300 K and all of them are desorbed already at 800 K, leaving behind a stable C_2H_4Ti$_2$ molecule. This prediction suggests that all the stored hydrogen molecules can be discharged easily through heating.

We next discuss the possibility of the dimerization and polymerization in the course of recycling and its effect on the hydrogen storage capacity. We found that two molecules can form a dimer through a Ti-Ti bond as shown in Fig. 4(a). The dimer formation is exothermic with an energy gain of E_D=2.28 eV, and leads to a

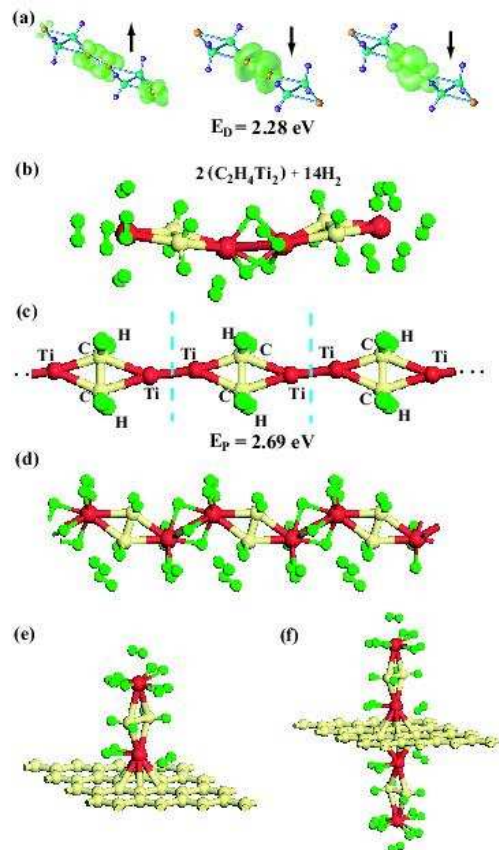FIG. 4: (color online) (a) Atomic configuration and charge density plots of a dimer of C_2H_4Ti$_2$ molecules linked by two Ti atoms one from either molecule. Large, medium and small balls indicate titanium, carbon and hydrogen atoms, respectively. Charge density plots (from left to right) correspond to HOMO spin-up, and two spin-down states. (b) Atomic configuration of C_2H_4Ti$_2$ dimer holding 14 H_2 molecules, (c) Polymer of C_2H_4Ti$_2$ molecule with polymerization energy E_P. (d) Atomic configuration of the polymer holding 6 H_2 molecule. (e) A C_2H_4Ti$_2$ molecule adsorbed above the center of a hexagon in a (3×3) cell holding 7 H_2. (f) Two Ti-ethylene complexes adsorbed above and below the center of the same hexagon holding 14 H_2.

stable structure. The ground state is ferromagnetic with μ =6μ_B. While each Ti atoms at both ends of the dimer can bind 5 H_2 molecules, two linking Ti atoms can absorb only 4 H_2 totaling to 14 H_2 per dimer. As a result, the gravimetric density obtained by the dimer is lowered to $\sim$ 10 wt%. The total energy can be further lowered by adding more C_2H_4Ti$_2$ molecules to the dimer, and eventually by forming a paramagnetic polymer as shown in Fig. 4(c). The polymerization energy per molecule is calculated to be E_P=2.69 eV and the H_2 storage capacity is further lowered to 6.1 wt%. Polymerization did not change the binding energy of the H_2 on Ti-atom significantly and therefore should not affect the desorption temperature.

In order to prevent C_2H_4Ti$_2$ molecules to form a pos-

TABLE I: The binding energies (in eV) with respect to atomic and bulk energies of various metals (M). The last two rows indicate the maximum number of H_2 molecule bonded to each metal and its average binding energy (in eV).

Property/M	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Mo	W	Pd	Pt
E_B (M-atomic)	1.39	1.47	1.27	0.05	0.37	0.83	1.30	0.70	1.41	none	1.69	0.37	1.18	1.56	1.78
E_B(M-bulk)	-2.72	-3.66	-4.13	-3.57	-3.20	-1.74	-2.53	-2.19	-2.25	–	-4.44	-5.84	-7.18	-2.24	-3.56
max H_2/M	5	5	5	5	5	5	3	2	2	–	5	5	5	2	2
E_B(per H_2)	0.39	0.45	0.43	0.35	0.34	0.26	0.41	0.87	0.14	–	0.57	0.77	0.90	0.58	0.95

sible polymer phase during recycling, one can imagine to incorporate these TM-ethylene complexes in a nanoporous materials such as MOF[5] and carbide-derived carbons[6]. As an example, we consider a $C_2H_4Ti_2$ adsorbed above and below the center of a hexagon of a graphene layer. Here the graphene is taken as a prototype system which represents the internal structure of a carbon-based nanoporous material. We find that TM-ethylene complex can form stable structure with graphene surface. As shown in Fig. 4 (e) and (f), single and double $C_2H_4Ti_2$ molecules assembled on a 3×3 graphene layer can hold 7 and 14 H_2 with average binding energy of 0.43 and 0.41 eV/H_2, respectively. The binding energy of the $C_2H_4Ti_2$ molecule is found to be ~2 eV. The actual binding energy in nanoporous materials could be even higher due to curvature effects[18]. The maximum gravimetric density achieved in this present framework is 6.1 wt%

It is important to know if the results reported above for M=Ti hold for other metals. Therefore we are currently studying a large number of metals and the details will be published elsewhere[19]. Our initial results are summarized in Table I, which clearly indicates that most of the light TM atoms can be bound to ethylene and each of them can absorb up to 5 H_2 molecules. Scandium is the ideal case but for practical reasons Ti is the the best choice of elements. Cr binds very weakly while Zn does not bind at all to the C_2H_4 molecule. Interestingly, Zr forms stronger bonding with C_2H_4 than Ti and can absorb up to ten H_2 molecularly with an average binding energy of 0.6 eV. Heavier metals such as Pd and Pt can also form complexes with C_2H_4 but bind less hydrogen molecules with significantly stronger binding energy than Ti. Table I also gives the binding energies with respect to bulk metal energies. The negative value for E_B indicates endothermic reaction. Due to very low vapor pressure of many metals, it is probably better to use some metal-precursor to synthesize the structures predicted here.

In conclusion, we showed that an individual ethylene molecule functionalized by two light transition metals can bind up to ten hydrogen molecules via Dewar-Kubas interaction, reaching a gravimetric density as high as ~14 wt%. We propose to incorporate TM-ethylene complex into carbon-based nanoporous materials to avoid dimerization/polymerization during recycling. Our results open a new approach to high-capacity hydrogen storage materials discovery by functionalizing small organic molecules with light transition metals.

---

* Electronic address: ciraci@fen.bilkent.edu.tr

[1] See the special issue Towards a Hydrogen Economy, by R. Coontz and B Hanson, Science **305**, 957 (2004).

[2] G. W. Crabtree, M.S. Dresselhaus and M.V. Buchanan, Physics Today, 39 (December 2004).

[3] A. Zuttel, Materials Today **6**, 24 (2003).

[4] B. Bogdanovic et al. Adv. Mater. **15**, 1012 (2003).

[5] T. Yildirim and J. Hartman, Phys. Rev. Lett. **95**, 215504 (2005).

[6] Y. Gogotsi et al. J. Am. Chem. Soc. **127**, 16006 (2005).

[7] T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005).

[8] T. Yildirim, J. Iniguez and S. Ciraci, Phys. Rev. B**72** 153403 (2005).

[9] Y. Zhao et al. Phys. Rev. Lett. **94**, 155504 (2005).

[10] S. Dag, Y. Ozturk, S. Ciraci and T. Yildirim, Phys. Rev. B **72**, 155404 (2005).

[11] Y. Zhao et al. Chem. Phys. Lett. **425**, 273 (2006).

[12] N. Akman, E. Durgun, T. Yildirim and S. Ciraci, J. Phys: Condens. Matter, J. Phys.: Condens. Matter **18**, 9509 (2006)

[13] B. Kiran, A.K. Kandalam, and P. Jena, J. Chem. Phys. **124**, 224703 (2006).

[14] H. Lee, W. I. Choi, and J. Ihm, Phys. Rev. Lett. **97**, 056104 (2006).

[15] Metal Dihydrogen and Bond Complexes - Structure, Theory and Reactivity, edited by G.J. Kubas (Kluwer Academic/Plenum Pub. New York, 2001).

[16] Q. Sun, Q. Wang, P. Jena and Y. Kawazoe, J. Am Chem. Soc. **127**, 14582 (2005).

[17] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org. Part of the calculations have been confirmed by VASP software: G. Kresse, J. Hafner, Phys. Rev. B **47**, 558 (1993).

[18] O. Gulseren, T. Yildirim and S. Ciraci, Phys. Rev. Lett. **87**, 116802 (2001).

[19] W. Zhou, T. Yildirim, E. Durgun, and S. Ciraci, Phys. Rev. B (in preparation, 2006).